

HEAVILY DOPED SEMICONDUCTOR NANOPARTICLES

FIELD OF THE INVENTION

This invention relates to doped semiconductor nanoparticles.

BACKGROUND OF THE INVENTION

Doping of bulk semiconductors, the process of intentional introduction of impurity atoms into a crystal discovered back in the 1940s, is a key route for tuning their properties. Its introduction allowed the wide-spread application of semiconductors in electronic and electro-optic components [1]. Controlling the size and dimensionality of semiconductor structures is an additional powerful way to tune their properties via quantum confinement effects. In this respect, colloidal semiconductor nanocrystals have emerged as a family of materials with size dependent optical and electronic properties. Combined with their capability for wet-chemical processing, this has led to nanocrystal-based light emitting diodes, solar cells and transistor devices prepared via facile and scalable bottom-up approaches. Impurity doping in such colloidal nanocrystals still remains an open challenge [2]. From the synthesis side, the introduction of a few impurity atoms into a nanocrystal which contains only a few hundred atoms may lead to their expulsion to the surface [3-5] or compromise the crystal structure. This inherently creates a highly doped nanocrystal under strong quantum confinement, and the electronic and optical properties in such circumstances are still unresolved.

Several strategies have been employed so far for doping nanocrystals. Binding ligands on the nanoparticle surface, which can donate carriers, or electrochemical carrier injection, have been shown to yield n-type doping in semiconductor nanocrystal superlattices [6-8]. While of great interest, such remote doping differs from substitutional doping, which has been studied mainly for color center impurities [9] and magnetic impurities, notably Mn atoms [10,11], providing insight to the challenging chemistry [12]. It should be noted, that despite efforts to concentrate such doping solely in the nanocrystal, significant amounts of the dopant materials were found associated with the nanocrystals surface.

Introduction of dopant precursors at specific stages of nanoparticle growth were effective in controlling the impurity location [13]. More recently, some progress has been made towards producing n-type CdSe quantum-dots (QDs) using tin and indium impurities [14, 15], and p-type InP using Cu impurities [16].

REFERENCE

- [1] S. M. Sze, *Physics of Semiconductor Devices* (Wiley-Interscience, New York ed. 2nd, 1981
- [2] D. J. Norris, A. L. Efros, S. C. Erwin, *Science* 319, 1776 (2008).
- [3] D. Turnbull, *Journal of Applied Physics* 21, 1022 (1950).
- [4] G. M. Dalpian, J. R. Chelikowsky, *Physical Review Letters* 96, 226802 (2006).
- [5] T. L. Chan, M. L. Tiago, E. Kaxiras, J. R. Chelikowsky, *Nano Letters* 8, 596 (2007).
- [6] M. Shim, P. Guyot-Sionnest, *Nature* 407, 981 (2000).
- [7] C. J. Wang, M. Shim, P. Guyot-Sionnest, *Science* 291, 2390 (2001).

- [8] D. Yu, C. J. Wang, P. Guyot-Sionnest, *Science* 300, 1277 (2003).
- [9] N. Pradhan, D. Goorskey, J. Thessing, X. Peng, *Journal of the American Chemical Society* 127, 17586 (2005).
- [10] R. N. Bhargava, D. Gallagher, X. Hong, A. Nurmikko, *Physical Review Letters* 72, 416 (1994).
- [11] C. A. Stowell, R. J. Wiecek, A. E. Saunders, B. A. Korgel, *Nano Letters* 3, 1441 (2003).
- [12] S. C. Erwin et al., *Nature* 436, 91 (2005).
- [13] Y. Yang, O. Chen, A. Angerhofer, Y. C. Cao, *Journal of the American Chemical Society* 128, 12428 (2006).
- [14] C. Tuinenga, J. Jasinski, T. Iwamoto, V. Chikan, *ACS Nano* 2, 1411 (2008).
- [15] S. Roy et al., *The Journal of Physical Chemistry C* 113, 13008 (2009).
- [16] R. Xie, X. Peng, *Journal of the American Chemical Society* 131, 10645 (2009).
- [17] T. Mokari, A. Aharoni, I. Popov, U. Banin, *Angewandte Chemie International Ed.* 45, 8001 (2006).

SUMMARY OF THE INVENTION

Doping of semiconductor materials by impurity atoms enables their widespread application in micro- and optoelectronics. However, for strongly confined colloidal semiconductor nanocrystals, doping has proven elusive. This arises both from the synthetic challenge of how to introduce single impurities and from a lack of fundamental understanding of this heavily doped limit under strong quantum confinement. Herein, provided are heavily doped colloidal semiconductor nanocrystals and a process for their preparation, namely for intentionally introducing (doping) an impurity such as metal atoms/ions impurities, generally referred to as a dopant material, to semiconductor nanoparticles, providing control of band gap, Fermi energy and presence of charge carriers. A combination of optical measurements, scanning tunneling spectroscopy and theory reveal the emergence of a confined impurity band and band-tailing. Successful control of doping provided n- and p-doped semiconductor nanoparticles which greatly enhance the potential application of such materials in solar cells, thin-film transistors, opto-electronic devices and other devices and applications.

Thus, the invention generally provides a nanoparticle of a material comprising a semiconductor material (herein referred to as the nanoparticle material), the semiconductor material being doped with at least one dopant material (two or more atoms thereof), wherein said dopant material is dispersed within said semiconductor material so as to alter the density of states of said nanoparticle material.

In one aspect of the invention, there is provided a nanoparticle material comprising a semiconductor material, the semiconductor material being doped with at least two atoms of a dopant material, wherein said at least two atoms of a dopant material are dispersed within said semiconductor material, inducing charge carriers in said nanoparticle material (in the regime of heavy doping in which the impurities charge carriers interact with each other).

In another aspect, a nanoparticle is provided, comprising a semiconductor material, the semiconductor material being doped with at least two atoms of a dopant material, wherein said atoms of the dopant material are heterovalent to atoms of the semiconductor material, said at least two atoms of a dopant material being dispersed within said semiconductor material.

The invention also provides a nanoparticle comprising a semiconductor material, the semiconductor material being doped with at least two atoms of a dopant material, wherein